

and which to some may appear too minute. But the uselessness of summarizing memoirs which, containing no facts essentially new, simply set forth considerations to which can be attributed only a historical interest, is also evident.

To the same period of time belong various works of an essentially technical nature and several patents. Of these, though of little value, I shall give an account later, when speaking of the industrial applications of the process of cementation.

## CHAPTER II

### STUDIES ON THE PROCESS OF CEMENTATION DURING THE LAST TWENTY YEARS OF THE NINETEENTH CENTURY

The first period of scientific investigations on the process of cementation, which I have briefly summarized in the preceding pages, a period notable more for the activity of the researches and the vivacity of the polemics than for clear and certain results, is followed by a second, also of twenty years' duration, during which but few new experimental data of real importance were brought out in support of one or the other of the various opposing hypotheses which in the preceding twenty years had been considered by their adherents as conclusively proved.

Leaving aside what concerns the advances in the technique of cementation, with which we shall deal later, I shall summarize briefly in this chapter the results of the principal scientific studies on the process of cementation published during the last twenty years of the nineteenth century.

A first work, due to Alb. Colson, is published in the *Comptes Rendus de l'Académie des Sciences*.<sup>1</sup> It contains no data essentially new as far as the process of cementation proper is concerned, that is, the diffusion of carbon into iron. The author tries, instead, to study the reciprocal action of iron and of carbon from a wider point of view, and believes that he can establish with certainty that, in the process of cementation, the diffusion of the carbon into the iron is accompanied by the reciprocal phenomenon of the diffusion of the iron into the carbon. According to the investigations of Colson, at relatively low temperatures (the phenomenon manifests itself even at 250° C.) the process of diffusion of the iron into the carbon is predominant, while at high temperatures the reciprocal process of diffusion of the carbon into the iron, that is, cementation proper, prevails. Since the author occupies himself especially with the first process, which takes place to a marked degree only at temperatures at which the process of cementation certainly does not occur to an appreciable extent, his work (in which he uses not very convincing reasoning by analogy) is of but slight interest for the study of the process of cementation.

In an interesting work published in the same year, by Forquignon,<sup>2</sup> under the title "Recherches sur la fonte malléable et sur le recuit des aciers,"

<sup>1</sup> 1881, 2nd sem., Vol. XCIII, pp. 1074-1076.

<sup>2</sup> *Annales de Chimie et de Physique*, Series V, Vol. XXIII (1881), pp. 433-554.



we find an interesting observation, the importance of which we shall have occasion to see later. This observation, from which Forquignon himself was unable to draw any useful conclusion, either because executed under conditions not definite enough or because various theoretical data relative to analogous phenomena were not then known, relates to a process of *decarburization (refining)* clearly observed in a cast iron *ignited with powdered carbon*, that is, subjected to the same treatment which gives rise to the *carburization* of steel.

Finally, R. Sydney Marsden presented at a meeting of the Chemical Society held on January 20, 1881, a memoir with the title "New Theory of the Conversion of Bar Iron into Steel by the Cementation Process." According to this *new theory*, the process of cementation is due to the diffusion of the carbon "in the form of *impalpable powder*" into the bars of iron, which, under the action of the high temperature, are "in an expanded and softened state." The diffusion of silicon is due to an analogous process.

I have cited this hypothesis, the improbability of which is clear, only because it shows plainly how at that time new efforts were being made to find an explanation of the process of cementation more satisfactory than those proposed in the preceding years.

Four years later, W. Hempel, in a memoir entitled *Ueber das Verhalten der verschiedenen Modificationen des Kohlenstoffs gegen Eisen bei hoher Temperatur*,<sup>1</sup> maintains that he has been able to prove experimentally that the diamond exercises a carburizing action on iron beginning at a temperature considerably lower than the other modifications of carbon.

According to Hempel, then, carbon does not cement iron at temperatures lower than red heat when the iron and the carbon, placed in contact, are heated in an atmosphere of nitrogen freed from the least trace of oxygen.

The investigations of Hempel can be considered as having only slight value, at least in so far as concerns the determination of the intervals of temperature between which the various phenomena are *localized*. To become convinced of this, it is sufficient to observe that Hempel determines the temperatures by means of a series of sheets of alloys of gold and platinum fusible at different temperatures. That the temperatures thus determined are anything but exact is clear when some of the results obtained by Hempel are compared with data at present known with certainty (and which we shall note later). Thus, for example, according to Hempel the lowest temperature at which the diamond carburizes iron is 1160° C.; the carburizing action of amorphous carbon on iron begins between 1385° and 1420° C., and results in the partial transformation of the iron into gray cast iron; at temperatures below 1380° C. amorphous carbon produces no carburization of iron whatever, while above 1420° this carburization is easily effected, always giving rise to the formation of gray cast iron.

<sup>1</sup> *Berichte der Deutschen Chemischen Gesellschaft*, 1885, Vol. I, pp. 998-1001.

The memoir of Hempel concludes with a series of considerations, not very convincing, in truth, or at least premature, on the differences which exist between the behavior of "white carbon" (diamond) and that of amorphous carbon, and on the analogies which exist between these and the differences in behavior which distinguish white phosphorus from red phosphorus.

In a brief memoir presented in 1890 before the Iron and Steel Institute,<sup>1</sup> W. C. Roberts-Austen reports the results of some experiments analogous to those of Hempel but carried out by heating electrolytic iron in contact with a diamond *in a vacuum*, instead of in an atmosphere of nitrogen, by means of an electric current. Under these conditions the carburization of the iron manifests itself only at intense redness, and then appears even if the iron, before being placed in contact with the diamond, is first heated a long time in a vacuum so as to free it from occluded gases.

From these experiments Roberts-Austen draws the simple conclusion—in truth very *prudent*—that whoever wishes to maintain that the intervention of a third substance is necessary to produce the *combination* of iron with carbon must necessarily assume that to produce to a considerable degree this effect minimum *traces* of such substances are sufficient, such as the traces of gaseous substances which can still remain occluded in the iron, notwithstanding the careful treatment to which this iron was subjected to remove the gases dissolved in it.

In the course of the interesting discussion which followed the reading of Roberts-Austen's memoir, G. J. Snelus called attention to the fact that the direct union of carbon with iron appears analogous rather to a process of *solution* than to a true combination proper,<sup>2</sup> and Sir Lowthian Bell reported the results of some of his experiments consisting in heating to redness for about a month a piece of cast iron and one of wrought iron placed in contact with each other along two perfectly plane surfaces, closely pressed against each other and covered with sand. But the fact observed by Bell, that a considerable quantity of the carbon passed from the cast iron to the iron, does not constitute a certain proof that carbon can diffuse into iron without the intervention of gases, for the conditions of the experiment were certainly not such as to insure sufficiently the exclusion of gases.

In the course of this same discussion, Roberts-Austen adds the observation that the product obtained by him by carburizing iron with a diamond contained both free carbon and combined carbon.

A year later Osmond presented before the "Académie des Sciences"<sup>3</sup> a Note in which, admitting as proved (by the experiments of Roberts-Austen just cited) that the diamond can carburize iron directly, without the inter-

<sup>1</sup> *The Journal of the Iron and Steel Institute*, 1890, Vol. I, pp. 81-84 and 91-96.

<sup>2</sup> We shall see that the process in question has at the same time the characteristics of a combination and of a solution.

<sup>3</sup> *Comptes Rendus*, 1891, 1st sem., Vol. CXII, pp. 578-580.



vention of gaseous substances, he proposed to study the *mechanism* of the carburization of iron by means of the diamond, and to determine the interval of temperature within which this carburization is effected.

Working in a current of very pure hydrogen, and using pure electrolytic iron, and diamonds ignited at redness and allowed to digest on the steam bath in hydrofluoric acid, Osmond obtains the following results:

1. At temperatures of 1035–1065° C., the carburization, determined by means of the microscope, attains in the mass of the iron a depth of 0.2 to 0.3 mm., remaining localized around the points of contact of the sheets of iron with the diamonds.

2. At temperatures of 1085°–1125° C., the diamonds (used in the proportion of 4 % with respect to the iron) completely dissolve in the iron, which melts, forming an ingot of *white cast iron*.

3. Still working at temperatures of 1085°–1125° C., but using a quantity of diamonds equal to 8% of the iron, Osmond obtains (although the temperature of fusion of gray cast iron is not reached) a *fused* ingot of *gray cast iron* to which adhere three fragments of blackened diamonds, covered with a graphitic patina containing iron. The iron has therefore served as intermediary in the formation of the graphite.

From these results Osmond draws the following conclusions:

1. The diamond, as such, does not cement iron, but when placed in contact with this metal at a high temperature it first undergoes a *molecular transformation* which renders it capable of cementing.

2. The diffusion of the carbon into the iron has, as a corollary, a diffusion of the iron into the transformed diamond. This confirms, under somewhat different conditions, the observations of Colson to which we referred in the preceding pages.

As can be seen, the observations of Osmond, like many of those carried out by other experimenters during the period with which we are now dealing, are of exclusively theoretical interest.

To investigations of a very different order, which, however, do not seem to have been susceptible of useful practical applications, belong some experiments, the results of which are briefly reported in a Note presented in 1892 by Jules Garnier before the "Académie des Sciences" of Paris.<sup>1</sup>

It seems well to me to make mention of these results because, together with a few others, they comprise all that has been published concerning a series of processes for which were taken out numerous patents based on mysterious descriptions and claiming marvellous results.

The first of Garnier's experiments consists in heating a tube of refractory material, placed horizontally in a reverberatory furnace, to a temperature between about 900° and 1000° C. In the tube is placed a bar of retort carbon,

<sup>1</sup> Jules Garnier, *Action de l'électricité sur la carburation du fer par cémentation* (*Comptes Rendus*, 1893, 1st sem., Vol. CXVI).

one end of which extends into the central and hottest part of the tube and there touches the end of another similar bar of soft steel (with 0.1% of carbon). The other end of the bar of carbon is connected electrically with the positive pole of a continuous current generator (Gramme machine) whose negative pole is connected with the end of the steel bar which extends toward the opposite end of the refractory tube.

By passing through the circuit thus established a current of 55 amperes with a tension of 7 volts (probably measured from the ends of the system composed of the two bars) and continuing the operation for three hours (always at a temperature of about 900°–1000° C.), Garnier obtained in the bar of iron a cemented zone 10 mm. thick. As is seen, the result is really noteworthy.

On substituting for the bar of retort carbon another bar of soft steel and placing between the two projecting ends of the two bars of steel, kept at a distance of about 1 cm., a little ground and compressed wood charcoal, at the end of the operation, conducted in the manner indicated above, only the bar acting as cathode was found to be cemented.

I do not find that further results of investigations analogous to these have been published.

In a brief Note presented at a meeting of the Iron and Steel Institute in May, 1896,<sup>1</sup> W. C. Roberts-Austen, after tracing briefly the history of scientific investigations on the process of cementation of steel, adds a few interesting considerations:

He begins by asserting that, on the basis of the experiments of Margueritte (see pp. 8–13), of Hempel (pp. 26–27), of Osmond (see p. 27) and of his own, it must be considered as proved that the process of cementation of steel is a true phenomenon of diffusion "by contact" of the solid carbon into the iron, analogous to the process of diffusion of salt into water or of that of the diffusion of gold or of platinum into solid lead.<sup>2</sup> Granted this, Roberts-Austen notes how the determination of the *way* in which the diffusion of the carbon into the iron takes place would without doubt be a study of the greatest practical interest in view of the ever increasing technical importance of the process of cementation.

Roberts-Austen reproduces a curve (see Fig. 11), representing the variation in the concentration of the carbon in the successive layers of a carburized zone, obtained by subjecting a wheel steel, with 0.26% of carbon, to cementation by the Harvey process. Concerning the conditions of the cementation, the author gives no detailed indications. In the form of this curve, which the author declares is similar to the curves traced by him from analogous data determining the course of the diffusion of gold or of platinum into solid lead,

<sup>1</sup> *The Journal of the Iron and Steel Institute*, 1896, Vol. I, pp. 139–142.

<sup>2</sup> This latter process had already formed the object of most interesting experimental researches, carried out by Roberts-Austen himself (see *Phil. Trans.*, 1896, p. 383).



Roberts-Austen sees a confirmation of his earlier observations, and especially of the conclusion that the technical process of cementation is effected by simple diffusion of the *solid* carbon into the *solid* iron with which it is placed in contact, without the intervention of gaseous carburizing substances.<sup>1</sup>

We shall see later how the conclusions which Roberts-Austen draws from the examination of this curve and of the two or three analogous ones observed by him later are not at all in accordance with the surer deductions drawn from the observation of many curves relative to cemented zones obtained by working under conditions which are simpler, can be determined with greater accuracy, and vary between wider limits.

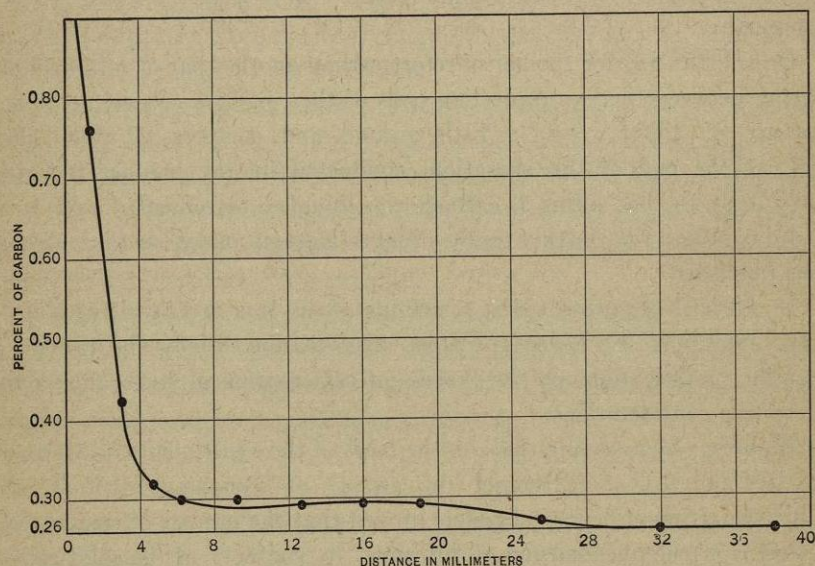


FIG. 11.

Continuing the summary review of the scientific investigations on the process of the diffusion of carbon into iron, we find a few experimental observations inserted by Royston in a work of his of more general nature, published under the title: *The Relation of Carbon to Iron at High Temperature*.<sup>2</sup> In the fifth chapter of his memoir Royston says that, having heated for twelve hours at 900° in a vacuum, in the same porcelain tube, two bars of

<sup>1</sup>In the preceding year, Behrens, on the basis of experiments described in a Note abstracted in the *Journal of the Iron and Steel Institute* (1895, Vol. II, p. 504), had again arrived at the opposite conclusion of the necessity of the intervention of carbon monoxide as "carrier" of the carbon in the process of cementation. As is seen, the explicit and absolute assertion, by different investigators, of the correctness, now of one, now of the other, of the two extreme and fundamentally opposed hypotheses, continues in this and continued in the following period. This interesting fact I shall take up shortly.

<sup>2</sup>*The Journal of the Iron and Steel Institute*, 1897, Vol. I, p. 166.

soft steel with 0.15% of carbon together with a bar of hard steel with 0.95% of carbon, he was unable to observe any change in weight or in carbon content in the bars whenever these bars were so placed that they were not in contact with each other. On the other hand, working under the same conditions but placing the more highly carburized bar between the other two and in contact with them, he found that the aggregate mean carbon content of the first bar had decreased to 0.42%, while that of the other two had increased, rising from 0.15% to 0.29%. This experiment proved, evidently, the correctness of the hypothesis according to which carbon diffuses into iron, as in solutions, by simple difference in concentration and without the necessity of the intervention of gases.

Together with various other observations on the limits of solubility of carbon in iron at various temperatures (observations on the basis of which he regards as confirmed the existence of the two carbides  $Fe_{14}C$  and  $Fe_{24}C$ , already announced by others but later recognized as being non-existent), Royston maintains that below the temperature corresponding to the point  $Ar_1$  carbon no longer tends to diffuse into iron. We shall see later how this conclusion has also been confirmed by more recent experiments.

To the argument, already considered by Royston in the work just cited, of the limit of saturation of *solid* solutions of carbon in iron, Saniter returns in a memoir presented at the next meeting of the Iron and Steel Institute.<sup>1</sup> This limit of saturation, which at a temperature of 700° C. corresponds, according to Royston, to 6.9% of carbon, reaches at 900° C., according to the experiments of Saniter, the value of 2.95%. In the experiments of Saniter, carried out by heating at 900° C. wire of soft steel in contact with wood charcoal for more than twenty hours, 0.53% of the carbon passed into the graphitic state.

We shall see later how recent studies on the conditions of equilibrium in systems consisting of the carburizing mixtures used as cements and of cementite—free or in the state of solid solution in  $\gamma$ -iron—throw a clear light on the causes of the contradictory results obtained from the experiments performed with the object of establishing the maximum limit of the concentration of carbon in iron obtainable by means of the process of cementation. The new views on this subject will also show the small practical importance of investigations of such a kind.

Moreover, already in the course of the long discussion, oral and written, which followed the reading of Saniter's memoir, Osmond set forth on this proposition some considerations which, within the limits of the then incomplete knowledge of the conditions of equilibrium in the system iron-carbon, cautioned against conclusions drawn too boldly from the results of determinations of the solubility of carbon in solid iron at high temperatures.

<sup>1</sup>H. Saniter, *Carbon and Iron* (*The Journal of the Iron and Steel Institute*, 1897, Vol. II, p. 115).



Osmond observes first that the limit of carburization of solid iron at a given temperature merely represents the solubility of the carbide  $\text{Fe}_3\text{C}$  in solid iron at that temperature. This limit, at the temperature of recalescence (about  $670^\circ$ ), seems to correspond to a carbon content of about 0.9%, and increases with rise in temperature. If every limit of carburization should correspond to a definite compound (which some authors seem to admit) there would have to be an infinite series of such compounds, which would be in contradiction to the nature of definite chemical compounds. In practice, then, the experimental determination of the limit of carburization at a given temperature could be carried out by means of direct cementation experiments only on condition of maintaining the temperature rigorously constant during the entire duration of the experiment. In fact, every slight lowering of the temperature would produce the precipitation of a certain quantity of cementite, so that from the total quantity of cementite found in the steel at the end of the cementation it would be necessary to subtract the quantity separated during the cementation as the result of oscillations in the temperature. Moreover, the dissociation of the carbide  $\text{Fe}_3\text{C}$  and the eventual formation of graphite complicate the phenomenon still more.

A year later J. O. Arnold read at the fall meeting of the Iron and Steel Institute (Stockholm, 1898) an interesting memoir on the "Microchemistry of Cementation."<sup>1</sup> This memoir has essentially as its object the study of the processes of carburization which are applied in the industry, of the production of hard steels of superior quality from the purer wrought irons by means of total cementation and subsequent crucible fusion or simple forging. I shall have occasion to refer to some of the data contained in this memoir when, later, I give a review of the industry just mentioned.

After an interesting notice on the data and methods followed in England in the industrial application of cementation to the total conversion of wrought irons into steels of various grades, Arnold reports a series of data relative to the microstructure and the chemical composition of the successive layers of eight cemented bars, belonging to the various "grades" established empirically by English manufacturers, on the basis of the "mean" carbon content of these bars.

As far as the microscopical examination of the cemented bars is concerned, the results of Arnold's observation do not throw much new light on the theory of the process of cementation. The author, in fact, limits himself essentially to bringing out how the proportion of cementite decreases in every bar from the periphery to the center and is the greater the longer the bars are cemented, conclusions which (even taking into account only what was known of the metallography of steels at the time of the publication of Arnold's memoir) are but an immediate and necessary consequence of the chemical analyses

<sup>1</sup>The *Microchemistry of Cementation*. *The Journal of the Iron and Steel Institute*, 1898, Vol. II, p. 185.

made on the successive strata of the bars observed. And from the micrography, carried out by Arnold with great care and great ability, various interesting conclusions might have been drawn to which chemical analyses could not have led, because they were carried out on successive layers of too great thickness. Thus, to cite but one case, in one of Arnold's micrographs (the sixth) appears most clearly the sudden variation in the concentration of carbon which manifests itself at the point corresponding to the surface of contact between the hyper-eutectic stratum and the eutectic stratum in a cemented zone. We shall see later the practical importance of this fact.

The microscopic observations which I have just cited are thus but confirmations of the results of the quantitative determinations of carbon made by Arnold on the successive layers (0.02 to 0.04 inch thick) of the cemented bars of the various "grades," and, in turn, the conclusions drawn from these results are limited to the establishment that in the deeply ("core") cemented bars the concentration of the carbon is nearly uniform throughout the whole metallic mass, while in the bars only superficially cemented the carbon content diminishes rapidly from the surface layers to those which are deeper. For these latter bars Arnold notes briefly in a table the existence of two or three distinct strata, but the description and the photographic reproduction which he gives of the microstructure of these strata exclude the coincidence of these with the three characteristic strata (hypo-eutectic, eutectic, hyper-eutectic) which I shall take up later.

The results of the carbon determinations are collected by Arnold into four diagrams (diagrams which, in what follows, I shall call simply *concentration-depth diagrams*), in which the distances of the median surfaces of the analyzed strata from the external surface of the steel bar are plotted as abscissas while the ordinates are proportional to the carbon content of each layer. I do not reproduce these diagrams here, because Arnold does not (nor could he) draw from them any but the very simple conclusions which are briefly reviewed above.

Arnold's memoir concludes with some brief "physical considerations" in which the author, after premising that the experimental conditions (exclusively industrial) under which he carried out the cementations to which the data contained in his memoir refer are not sufficiently well-defined to base thereon theoretical considerations, announces that the results of more accurate investigations, carried out by him with A. MacWilliam, now permit him to assert that the diffusion of carbon in the process of cementation takes place by way of two distinct varieties of *interpenetration*, the first of which begins at the temperature of  $\text{Ar}_2$  (about  $750^\circ \text{C.}$ ), between pure iron and the "substance"  $\text{Fe}_{24}\text{C}$ , while the second takes place only at temperatures above  $950^\circ \text{C.}$ , between the normal carbide  $\text{Fe}_3\text{C}$  and the "subcarbide"  $\text{Fe}_{24}\text{C}$ .

This hypothesis explains also, according to Arnold (and this observation is analogous to one of Royston to which I have already referred), the fact that at the temperature of  $800^\circ$  it is not possible to increase carburization by



cementation beyond 0.9% of carbon (a value corresponding to the "compound"  $\text{Fe}_{24}\text{C}$ ) and to obtain more highly carburized steels it is necessary to carry out the cementation at temperatures above  $950^{\circ}\text{C}$ .

The reading of Arnold's memoir was followed by a brief discussion, in which Roberts-Austen declares that Arnold's hypothesis, based on the existence of the two distinct carbides  $\text{Fe}_{24}\text{C}$  and  $\text{Fe}_3\text{C}$ , has little probability; he considers, on the other hand, more probable the hypothesis (which, as we have seen, had already been proposed by him) that the diffusion of carbon into solid steel is a phenomenon entirely analogous to that of the diffusion of a salt into water. J. E. Stead adds some observations on the phenomenon of the "agglomeration" of cementite which is manifested in the prolonged heating of steels subjected to cementation.

The results of the more accurate investigations of Arnold and of MacWilliam, stated in the memoir of Arnold which I have just summarized, form the subject of another paper, presented also before the Iron and Steel Institute, in the following year.<sup>1</sup> Of this I think it well to give a rather detailed summary.

After a brief historical introduction, in which are mentioned the principal of the earlier researches on the diffusion of carbon into iron (Bell, Royston, Osmond), of iron sulphides into iron (Campbell), and of gold into lead (Roberts-Austen), the authors describe minutely the experimental methods adopted by them for the exact quantitative determination, chemical and micrographical, of the "molecular migration" of the various elements into steel.

The greater part of the experiments were arranged as indicated in Fig. 12. In a cylinder of almost pure iron, 3 inches long and 0.7 inch in diameter, was bored an axial hole, exactly cylindrical and well polished, 0.35 inch in diameter. Other cylinders of iron containing about 1.5% of the elements whose diffusive power was to be determined were then turned and adjusted and polished exactly to the diameter of the hole bored in the iron cylinder. Into the first hollow cylinder, heated to about  $150^{\circ}\text{C}$ . so as to expand the hole a little, was introduced one of the other cylinders, functioning as core, so that on cooling the "core" adhered perfectly to the "muff." In the core

<sup>1</sup> J. O. Arnold and A. MacWilliam, *The Diffusion of Elements in Iron* (The Journal of the Iron and Steel Institute, 1899, Vol. I, p. 85).

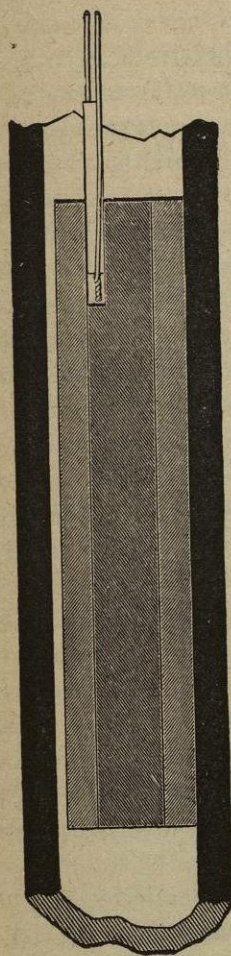


FIG. 12.

was bored a hole to receive the joint of a thermo-electric couple for the exact determination of the temperature of the system; the latter was then heated in a porcelain tube which had been evacuated as completely as possible.

After heating in a vacuum ten hours at a temperature between  $950^{\circ}$  and  $1050^{\circ}\text{C}$ ., the piece, after cooling, was again turned on the lathe and the material of the muff thus removed until there remained of it on the core but a layer one-twenty-fifth of an inch thick. Then the material of this layer was also removed, collected separately and analyzed to establish whether the foreign element contained in the core had penetrated into the muff.

On the basis of a first series of experiments, the results of which are collected in the following table, the authors divide the elements which are most frequently found in steels into two classes: "migratory elements" and "fixed elements."<sup>1</sup>

The microscopic examination of the pieces subjected to the treatment described, and numerous control experiments, confirmed the results summarized in the accompanying table.

Elements		Original percentage in the muff	Original percentage in the core	Percentage in the layer (1/25 inch) of the muff adjacent to the core after the treatment	Percentage passed by diffusion from the core to the muff in 10 hours
Migratory	Carbon.....	0.05	1.78	0.55	0.50
	Sulphur.....	0.02	0.97	0.12	0.10
	Phosphorus...	0.015	1.36	0.11	0.095
	Nickel.....	none	1.51	0.11	0.11
	Manganese...	0.05	1.29	0.04	none
	Silicon.....	0.027	1.94	0.028	none
Fixed	Chromium...	none	1.10	none	none
	Aluminium...	0.02	1.85	0.02	none
	Tungsten....	none	1.41	none	none
	Arsenic.....	0.02	1.57	0.012	none
	Copper.....	traces	1.81	traces	none

After some general considerations, on the basis of which (especially as far as the diffusion of phosphorus is concerned) it is shown to be possible that certain elements diffuse into iron, when hot, in the form of definite compounds with the iron itself, the authors propose to establish whether carbon diffuses into iron while remaining in the elementary (free) state or in the form of iron carbides, and they describe in detail experimental researches undertaken for this purpose.

Three preliminary experiments were carried out, following those already described, using three muffs of pure iron and three cores containing, respectively, 0.38%, 0.89% and 1.78% of carbon. After ten hours of heating at  $1000^{\circ}\text{C}$ . in a vacuum, from the three "compound" cylinders was removed on the

<sup>1</sup> We shall see later that, in practice, such a sharp distinction can not be made.



lathe the material of *eight* concentric layers (four from the muff and four from the core), the material of each layer being collected separately and analyzed.

The results of the carbon determinations on the eight layers of each of the three cylinders are represented schematically in Fig. 13 and reproduced

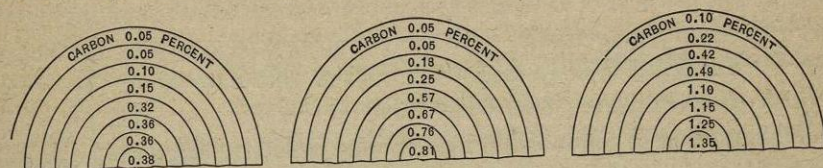


FIG. 13.

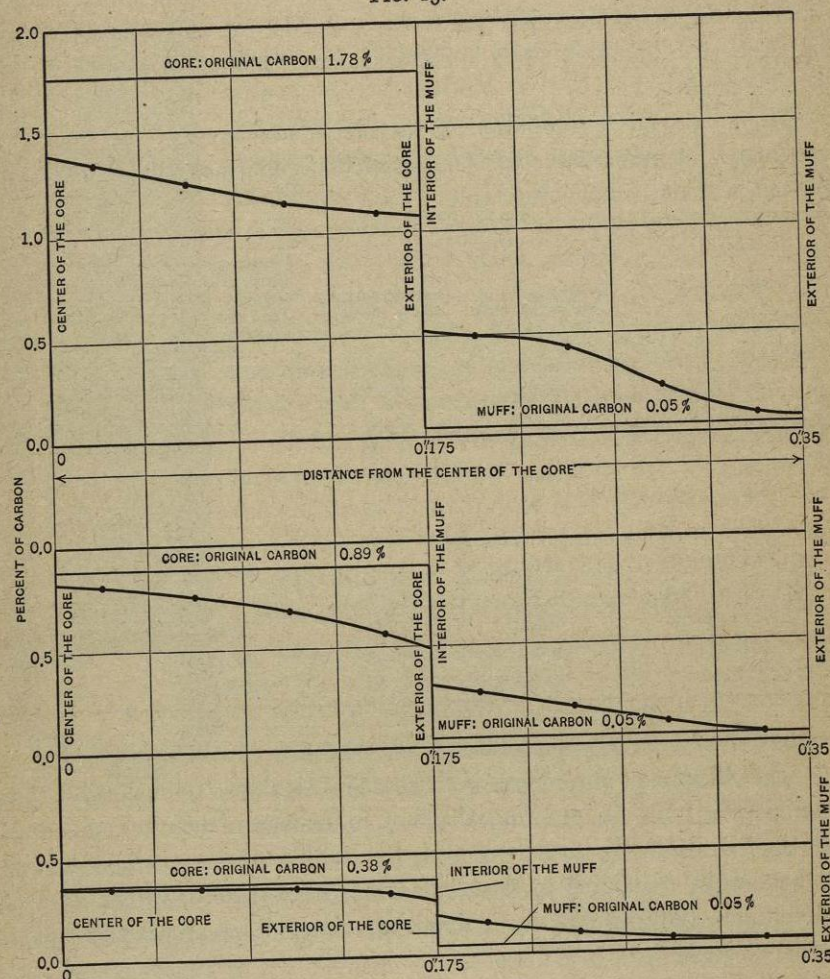


FIG. 14.

in three diagrams (Fig. 14), in which the abscissas represent the distances of each of the layers analyzed from the axis of the metallic cylinder and the ordinates are proportional to the corresponding concentrations of carbon resulting from the analysis of this layer.

From these first experiments the authors limit themselves to drawing the conclusion that the diffusion of the carbon from the core to the muff is the more rapid the higher the carbon content of the core, but they do not find that a simple relation exists between this percentage and the velocity of diffusion.

Another series of experiments, carried out under conditions entirely analogous but working at different temperatures and using successively muffs of iron containing varying percentages of carbon, furnished the results in the following table.

Percentage of carbon in the muff	Percentage of carbon in the core	Length of heating in vacuum (hours)	Temperature (save oscillations of a few degrees)	Percentage of carbon in the layer (1/25 inch) of the muff adjacent to the core after the treatment	Percentage of carbon migrated by diffusion in 6 hours
0.05	1.78	6	636° C.	0.05	none
0.05	1.78	6	739° C.	0.05	none
0.05	1.78	6	785° C.	0.16	0.11
0.05	1.78	6	855° C.	0.45	0.40
0.59	1.78	6	750° C.	0.76	0.17
0.59	1.78	6	850° C.	0.87	0.28
0.89	1.78	6	740° C.	0.87	none
0.89	1.78	6	850° C.	0.87	none
0.89	1.78	6	960° C.	1.20	0.31

Since the determination of the critical points of the metal (with 1.78% of carbon) forming the core shows that this metal undergoes its allotropic modifications at temperatures below 700° C., and does not suffer further transformations above this temperature, and since, on the other hand, the data in the last table show that the most marked variations in the diffusion velocity of the carbon appear at temperatures above 700° C., it is necessary to admit that these variations are due to the "molecular transformations" of the iron constituting the muff.

From the numbers in the table relative to the first two series of experiments (carried out with muffs containing, respectively, 0.05% and 0.59% of carbon) and taking into account the critical temperatures of the two materials constituting the muffs, the authors consider it as proved that the diffusion of the carbon occurs only at temperatures above those of the point  $Ar_2$  of the metal of the muff.

The results of the third series of experiments prove, then, that when the concentration of the carbon in the muff exceeds 0.89% (a concentration for which, according to a hypothesis advanced previously by Arnold, the steel consists entirely of the "subcarbide"  $Fe_2C$ ) the minimum temperature at which the diffusion can take place shows a sudden rise of 150° C. (from 750° to 900°).



Such a sudden rise is explained, according to the authors, by assuming that, until the concentration of the carbon in the muff falls below 0.89%, the carbon diffuses in the form of the carbide  $\text{Fe}_{24}\text{C}$ , at all temperatures above  $\text{Ar}_2$ , while as soon as the concentration reaches 0.89% and the entire muff consists of the "subcarbide"  $\text{Fe}_{24}\text{C}$ , then the carbon diffuses in the form of the carbide  $\text{Fe}_3\text{C}$ , which is the reason the diffusion can take place only at a temperature above  $900^\circ\text{C}$ . Inversely, then, the sudden variation in the minimum temperature of diffusion of carbon is, according to the authors, a proof that the carbon actually diffuses in the two cases in the form of the two different carbides.

For the results of this series of experiments also, the authors advance proofs based on the microscopical observation of sections normal to the axes of the various compound cylinders.

Having reached this point, the authors avail themselves of the experimental results obtained to advance a theoretical explanation which can mostly no longer be accepted to-day, since the non-existence of a definite carbide  $\text{Fe}_{24}\text{C}$  has been proved. They developed, however, some interesting considerations (confirmed, also, by new experiments) on the phenomenon of the diffusion of carbon manifesting itself in the various structural elements of steels during the heating which precedes tempering, and on the effects of such phenomena on the properties of the tempered steels. But the greater part of these considerations, too, though very ingenious, are based upon the supposed existence of the "subcarbide"  $\text{Fe}_{24}\text{C}$ ; they can not therefore be considered as correct to-day. Moreover, they concern only indirectly the mechanism of the process of cementation.

The memoir of Arnold and MacWilliam closes with some experiments on the diffusion of the sulphide and oxysulphide of iron through iron at high temperatures; the results of these experiments confirm those previously published by Campbell in proof of the great rapidity with which the diffusion of the oxysulphide is effected, and show that the sulphide of iron also, under analogous conditions, diffuses rapidly into iron.

In the discussion which followed the reading of the memoir of Arnold and MacWilliam, Stead raised some objections to the hypothesis that in the process of cementation carbon diffuses into the iron in the form of two definite compounds,  $\text{Fe}_{24}\text{C}$  and  $\text{Fe}_3\text{C}$ , and added some interesting observations (which I do not quote, as they bear only indirectly on the special argument which we are dealing with) on the experiments of the authors and the earlier ones of Campbell on the processes of diffusion of the sulphide and oxysulphide of iron.

Among the observations made by the different speakers in the course of this discussion, in which R. A. Hadfield, Harbord, Stansfield, H. Louis and Saladin participated, those of Harbord are especially interesting: Basing his remarks upon the analogy between the separation of cementite from steel and the crystallization of hydrates from saline solutions, he combats the hypothe-

sis that carbon diffuses into iron in the form of a definite carbide. The observations of Stansfield are based on the same comparison with the crystallization of saline solutions, observations still valid to-day, which bring out with extraordinary clearness the true course of the phenomena which take place during the cooling of steels, as appears on the basis of the most recent experiments, and oppose serious objections (recognized to-day as correct) to the theory of the existence of two distinct carbides of iron ( $\text{Fe}_{24}\text{C}$  and  $\text{Fe}_3\text{C}$ ), on which Arnold and MacWilliam base their explanation of the phenomena observed in their experiments. As to the fact observed by the two authors that in a steel with 0.05% of carbon the diffusion of the carbon does not take place to an appreciable extent except at temperatures above  $750^\circ$ , Stansfield explains it very easily and without having recourse to the hypotheses of Arnold and MacWilliam, observing that in such a steel, at  $700^\circ\text{C}$ ., only about 6% of the mass of the metal (and precisely that part which, in the cooled steel, constituted the pearlite) passes into a state of solid solution (into  $\beta$ -iron), distributed around the crystals of pure iron ( $\alpha$ -ferrite), so it is quite natural that under such conditions the diffusion of the carbon, occurring over such a small portion of the mass of the steel, should take place only to a small extent.

Stansfield concludes that further diffusion experiments, analogous to those of Arnold and MacWilliam, may furnish a useful method for determining the solubility curve of the carbide  $\text{Fe}_3\text{C}$ , a curve very difficult to trace by thermal methods.

H. Louis observes that the characteristic behavior of nickel diffusing into solid iron may be due to the formation of nickel carbonyl. He then adds a few observations on the behavior of phosphorus.

The report of the oral discussions, concluded by two very vivacious and not at all objective replies by Arnold and MacWilliam, is followed by two letters, the first of which, by T. W. Hogg, contains some interesting observations which bring out the practical importance of an accurate study of the diffusion of the various elements into steel as a basis for a better knowledge of the phenomena of liquation which manifest themselves in steel ingots.

The second letter, by E. H. Saniter, contains some observations on a possible hypothetical relation between the "diffusibility" of the various elements into solid steel and their atomic volume, and some considerations on the conditions of existence of iron carbides in solution in iron.

The memoir of Arnold and MacWilliam is abstracted fully by Ledebur in *Stahl und Eisen*, July 1, 1898, adding to the summary various considerations of his own.

Like Harbord and Saniter before him, Ledebur considers improbable, and not necessary for the explanation of the facts observed, the hypothesis of the existence of the definite subcarbide  $\text{Fe}_{24}\text{C}$ , assumed by Arnold and MacWilliam. Ledebur cannot understand why they seek to attribute to the



hypothetical existence of carbides the phenomena of the diffusion of carbon into solid iron, both in the case (used in the process of cementation) where the diffusion takes place by contact of the free carbon with the iron and in the case where the diffusion is effected between more highly carburized iron and that less carburized, placed in contact. He maintains that the same phenomena are explained very simply by the passage of the carbon "from the molecules which are richer in it to those which contain a smaller amount," by a process entirely analogous to that of diffusion in saline solutions.

### CHAPTER III

#### STUDIES ON THE PROCESS OF CEMENTATION DURING THE FIRST SEVEN YEARS OF THE TWENTIETH CENTURY

The last period of scientific studies on the process of the cementation of steel is clearly distinct from the preceding one, being characterized by the fact that the experimental researches comprised within it were almost always carried out with new and more accurate means of investigation, and interpreted on the basis of the new theories of physical chemistry.

Another fact characteristic of this period, which includes the first decade of our century, is the renewed activity in scientific researches on the cementation of steel, a fact which, however, is explained quite easily by the recent rapid development of the mechanical industries (and especially of the automobile industry) for which (as we shall see later) the process of cementation is becoming every day a more valuable and necessary aid.

The period with which we are now dealing can be divided into two well-defined parts:

In the first, which includes the first seven years, many of the old problems which we have seen in the preceding chapters studied and discussed for many years back, are subjected to new, ample and accurate investigations, carried out with new experimental methods and interpreted according to the new physicochemical doctrines. But the work of these first years, while preparing new and valuable experimental material, does not lead yet to the sure and complete solution of the problems studied so many years; among these it suffices to mention that of the definition of the function of solid cements and of gaseous cements, and that of the limits of temperature between which the process of cementation is effected.

In the second part of the same period, including approximately the last four years, several of the fundamental questions of the theory of cementation are completely solved in definite form, various important technical improvements of the process of cementation being based on their solution.

In the present chapter I shall limit myself to setting forth objectively the results of the experimental researches carried out during the first part of this last period, reserving the discussion of the possible theoretical and practical conclusions for one of the following chapters, together with those from the earlier investigations, summarized in the first two chapters, and of the later, more important ones, summarized in the fourth chapter.

Leaving aside some works of entirely secondary importance or of exclu-